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Local Nanostructured Ashes Synthesized by Incineration, Pulverization and Spectrophotometric Characterization of Solid Wastes Ashes for Use as Admixtures in Soil Stabilization

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Abstract

Nanostructured ash materials were locally synthesized by the spectrophotometric characterization method and applied in the stabilization of lateritic soils to evaluate the effect of the ashes on the strength properties of the lateritic soil. The ashes are products of the incineration and complete pulverization of some selected biodegerable solid waste materials. Results showed that the ashes were nanomaterials by size, reactive surface, absorbance and texture. And the studied soil was found to be an A-2-7 soil, according to AASHTO classification method. These ash materials were mixed with the soil in varying proportions of 3%, 6%, 9%, 12% and 15% by weight of dry soil and their respective effects on the soil evaluated. The California bearing ratio and unconfined compressive strength results improved remarkably. The results showed that the ash materials are good admixtures in the stabilization of lateritic soils in pavement sub-grade and sub-base construction and other civil engineering works. These materials are secured free of cost and by implication reduced the cost of stabilizing the lateritic soils hence a cost effective stabilization was achieved.

***Keywords**: Nanomaterials; Nanostructured Ash; Geotechnics; Nanosieve Characterisation; Soil Stabilization.*

1. Introduction

Local nanosized ash is a synthesized mass of particles achieved by incineration, pulverization and characterization which has an average size ranging between 0 and 999 nm for the purpose of Geotechnical engineering stabilization. These ashes can be classified as zero dimensional, 1 dimensional, 2 dimensional or 3 dimensional nanomaterials [1; 2]. They are synthesized from various waste materials for the purpose of engineering services [3]. In Nigeria, the disposal of waste materials from agricultural and industrial operations like palm bunch, cocoanut shell, palm kernel shell, used tyres, snail shell, animal bone, waste paper etc. has been a source of worry [4]. In recent times, these materials' ash has been used by researchers at the macro and micro scale to stabilize weak engineering soils [5; 6]. The results of these research works have shown remarkable improvement in the characterization, behaviour and strength properties of stabilized soils [6; 7]. In the developing countries, Nigeria, for example, solid waste disposal and management is a huge problem because they lack the training and technology to evaluate the effects of solid wastes or to recycle same as it is done in other advanced countries of the world [4]. The agencies and ministries whose responsibility it is to ensure effective management and disposal of solid waste are nowhere near the technological trend. These agencies include; Ministry of Environment, Ministry of Works, Ministry of Transport and Ministry of Urban Renewal and Planning. In a bid to save our environment, the Environmental Geotechnics experts have developed what may be considered an efficient technology through which solid wastes would be managed and disposed and also, save the Geoenvironmental decay taking place in every urban and rural dwelling especially in the southeastern part of Nigeria. These decays include pavement failure, gully erosion sites, slope failures, especially on road embankments, etc. The main aim of this work was to synthesize through Spectrophotometric analysis and use as soil stabilization admixtures, the solid waste ashes to rehabilitate our failed environment. The specific objectives were; (i) to ensure an efficient solid waste disposal and management in Umuahia, (ii) to characterize the soil and synthesized ashes through laboratory experiments (iii) to apply these solid wastes ashes to engineering stabilization works and (iv) to evaluate the effect of some selected solid waste materials ash on the behavior of stabilized soil for use in pavement and Environment Geotechnics works.

2. Materials and Methods

Selected solid waste materials, e.g. palm bunch, waste paper, palm kernel shell, vehicle tyre, coconut shell, snell shell, etc. were collected, sun dried, burnt and completely pulverized. The ashes were further nanosized by passing the collected powder through a nano filter or sieve of size 200 nm [8]. The above nanosized ashes were subjected to characterization by the UV-Vis spectrophotometric test to determine the following parameters; peak wavelength of machine at test (λ), degree of particle absorbance, full width of half maximum (β) and photometric diffraction angle (θ) [9]. The above technique is approached in various forms and procedures, giving varying degrees of accuracy and precision. The Debye-Scherrer's formula was thereafter applied to determine the average particle size (D) of the ashes under study, which many researchers have applied previously though on the synthesis of the well known conventional nanomaterials 1; 2; 10; 11; 12; 13; 14; 15; 16; 17; 18],

$$D = \frac{0.9\lambda}{\beta cos\theta} \qquad (1)$$

β is obtained from the corrected FWHM by convoluting Gaussian profile which models the specimen broadening β_r as follows; [2; 16; 17; 18] ;

$$\beta_r^2 = \beta_0^2 - \beta_i^2 \qquad (2)$$

Where, β_0 Is observed broadening and β_i Is instrumental broadening.

The chemical compound composition test was also conducted on the ash materials to determine their degree of pozzolanity; aluminates, silicates and ferrites contents and expected reactions between the compounds and soil elements. The ashes synthesized by spectrophotometric analysis were used to stabilize lateritic soils to evaluate their effect in the present form, on the properties of the lateritic soil for engineering purposes. And the strength characteristic tests were conducted to evaluate the effect of these ashes on the lateritic soil sample thus; the standard proctor compaction test, cassagrande consistency limits test, California bearing ratio test and the unconfined compressive strength test to [19; 20]

(a) ***Consistency Limits Tests:*** This was conducted at the Geotechnical and Materials Engineering laboratory, Department of Civil Engineering, Michael Okpara University of Agriculture,Umudike in accordance with BS 1377-2 [19]; BS 1924 [20]; BS 5930 [21]; NGS [22].

(b) ***Soil Compaction Test*:** This was conducted at the Geotechnical and Materials Engineering laboratory, Department of Civil Engineering, Michael Okpara University of Agriculture,Umudike in accordance with BS 1377-2 [19]; BS 1924 [20]; BS 5930 [21]; NGS [22].

(c) ***CBR Test***

This was conducted in the Niger Pet Geotechnical Enginering laboratory, Uyo, Akwa Ibom State, Nigeria on the natural soil sample as well as the stabilized samples with 3%, 6%, 9%, 12% and 15% percentage proportions of nano palm bunch ash in accordance with BS 1377-2 [19]; BS 1924 [20]; BS 5930 [21]; NGS [22].

(d) Unconfined Compressive Strength Test

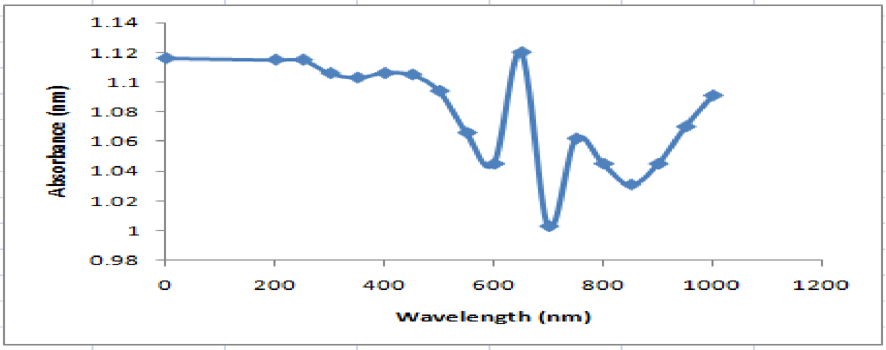
This was conducted at Niger Pet Geotechnical Engineering Laboratory, Uyo, Akwa Ibom State, Nigeria on the sample with admixture proportions of 3%, 6%, 9%, 12% and 15% in accordance with BS 1377-2 [19]; BS 1924 [20]; BS 5930 [21]; NGS [22] as shown in Figure 3.

(e) ***UV-VIS Spectrophotometric Test:*** the UV/VIS Spectrophotometer test at 25°C was conducted in accordance with BS 1377 [19] at the Chemistry lab of the Michael Okpara University of Agriculture, Umudike on both the soil and the admixture to determine their particle absorbance and average particle sizes.

3. Results and Discussion

Figures 1, 2, 3, 4, 5 and 6 show the variation of ash particle absorbance against wavelength for the Nanosized Palm Bunch Ash, Nanosized Waste Tyre Ash, Nanosized Waste Paper Ash, Nanosized Palm Kernel Shell Ash, Nanosized Snell Shell Ash and Nanosized Coconut Shell Ash particles respectivley using UV/VIS Spectrophotometer at 25^{0}C. From the exercise, it can be deduced that the maximum absorbance varied at different wavelengths at a full width of half maximum of 150m and exposure angle of 65°. The average particle sizes were estimated by Debye Scherrer expression (Eq. 1) shown in Table 1. The particle absorbance enhances the mechanism whereby size can potentially promote cohesion between the admixture, improve the van der waal's forces between particles and stabilized soil by presenting a larger reactive surface to achieve flocculation of the matrix, characterization of the molecular composition of organic matter in soil fundamental mass, lateral distribution of carbon forms in soil microaggregates, characterization of the composition of dissolved organic carbon in the ash during stabilization, etc. The nanopores of the ash material due to nanosization contribute 99% of the surface areas to the mixture homogeneity because it was less kinetically restricted at the temperature when its isotherm constructed during the mixing and stabilization mechanics.

Wavelength	Absorbance
0	1.116
200	1.115
250	1.115
300	1.106
350	1.103
400	1.106
450	1.105
500	1.094
550	1.066
600	1.045
650	1.12
700	1.003
750	1.062
800	1.045
850	1.031
900	1.045
950	1.07
1000	1.091



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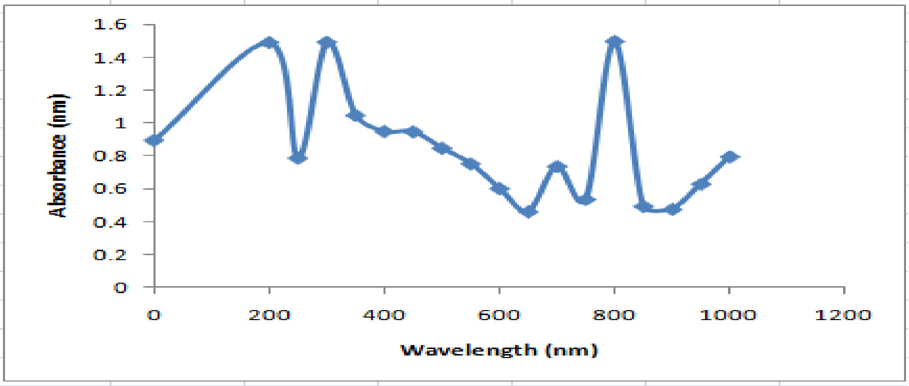
Number of Replicate: 3
Max. Absorbance: 1.120 nm at 650 nm wavelenght

Figure 1: Variation of Absorbance against wavelength for the Nanosized Palm Bunch Ash particles using UV/VIS Spectrophotometer at 25^{0}C [3]

Wavelength	Absorbance
0	0.897
200	1.491
250	0.789
300	1.493
350	1.049
400	0.951
450	0.949
500	0.849
550	0.754
600	0.604
650	0.463
700	0.738
750	0.538
800	1.498
850	0.496
900	0.478
950	0.631
1000	0.797



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Max. Absorbance: 1.498 nm at 800 nm wavelenght

Figure 2: Variation of Absorbance against wavelength for the Nanosized Waste Tyre Ash particles using UV/VIS Spectrophotometer at 25^{0}C

Wavelength	Absorbance	
0	1.016	
200	1.107	
250	1.015	
300	1.136	
350	1.103	
400	1.116	
450	1.005	
500	1.154	
550	1.166	
600	1.075	
650	1.102	
700	1.003	
750	1.062	
800	1.045	
850	1.031	Exp details
900	1.045	Re: mouau/chemlab/UV-VIS/sample 3/exp.003
950	1.07	Date Printed: 16:03:2017
1000	1.191	Number of Replicate: 3
		Max. Absorbance: 1.191 nm at 1000 nm wavelenght

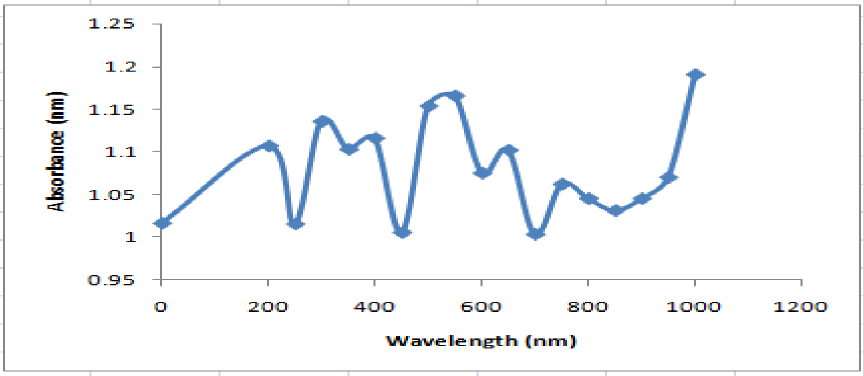

Figure 3: Variation of Absorbance against wavelength for the Nanosized Waste Paper Ash particles using UV/VIS Spectrophotometer at 25^{0}C

Wavelength	Absorbance	
0	1.216	
200	1.007	
250	0.015	
300	1.036	
350	0.903	
400	0.416	
450	1.005	
500	1.154	
550	1.216	
600	0.075	
650	0.102	
700	1.003	
750	1.212	
800	1.217	
850	0.931	Exp details
900	0.245	Re: mouau/chemlab/UV-VIS/sample 4/exp.003
950	1.07	Date Printed: 16:03:2017
1000	0.191	Number of Replicate: 3
		Max. Absorbance: 1.217 nm at 800 nm wavelenght

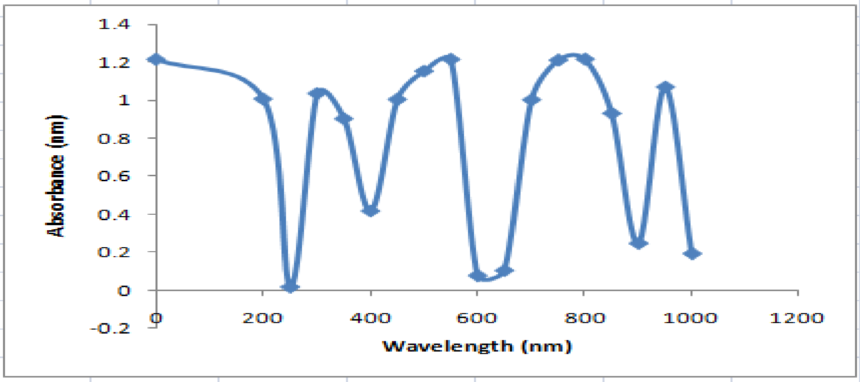

Figure 4: Variation of Absorbance against wavelength for the Nanosized Palm Kernel Shell Ash particles using UV/VIS Spectrophotometer at 25^{0}C

Wavelength	Absorbance
0	1.116
200	1.007
250	0.115
300	1.046
350	0.501
400	0.417
450	1.105
500	1.054
550	1.119
600	0.085
650	0.182
700	1.003
750	1.103
800	1.11
850	0.131
900	1.245
950	1.07
1000	0.081

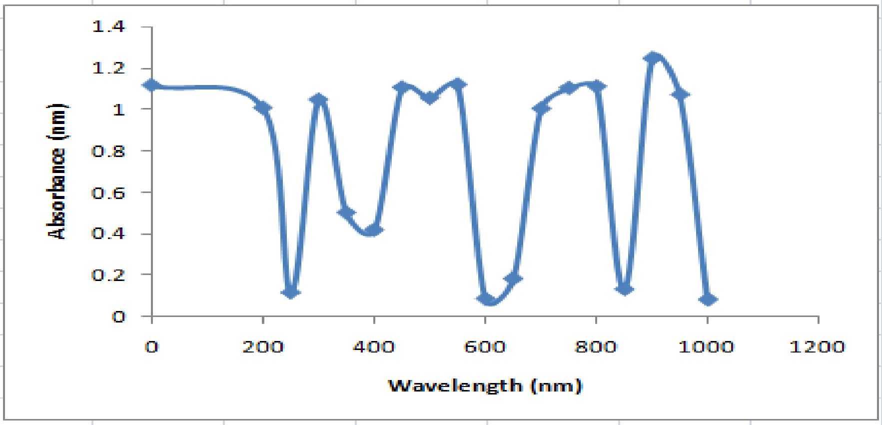

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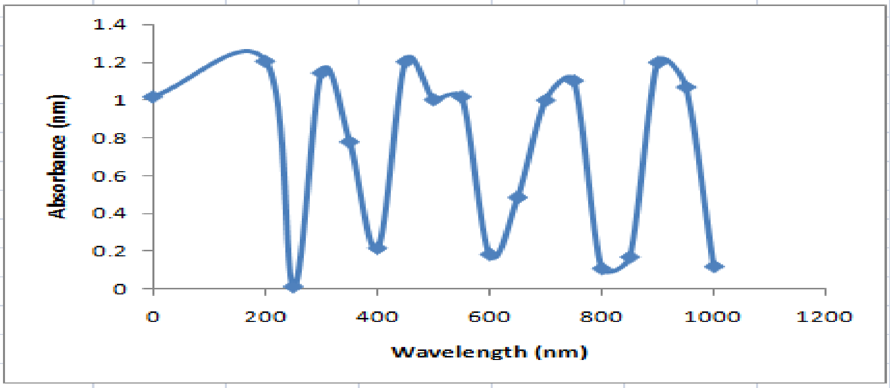
Figure 5: Variation of Absorbance against wavelength for the Nanosized Snell Shell Ash particles using UV/VIS Spectrophotometer at 25^0C

Wavelength	Absorbance
0	1.019
200	1.207
250	0.015
300	1.146
350	0.781
400	0.218
450	1.205
500	1.004
550	1.019
600	0.185
650	0.487
700	1.001
750	1.104
800	0.11
850	0.171
900	1.201
950	1.07
1000	0.121



Exp details
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Date Printed: 16:03:2017
Number of Replicate: 3
Max. Absorbance: 1.207 nm at 200 nm wavelenght

Figure 6: Variation of Absorbance against wavelength for the Nanosized Coconut Shell Ash particles using UV/VIS Spectrophotometer at 25^0C

Table 1: Average particle size from UV/VIS Spectrophotometer at 25^0C by Debye Scherrer

Ash	Absorbance (A), nm	Wavelength (λ), nm	Average Particle Size, nm
NPBA	1.120	650	9.223
NWTA	1.498	800	11.358
NWPA	1.191	1000	14.198
NPKA	1.217	800	11.358
NSSA	1.245	900	12.778
NCSA	1.207	200	2.840

*NPBA= nanosized palm bunch ash, NWTA= nanosized waste tyre ash, NWPA= nanosized waste paper ash, NPKA= nanosized palm kernel shell ash, NSSA= nanosized snell shell ash, NCSA= nanosized coconut shell ash.

Table 2 shows the compound composition and bonding potentials of the nanosized waste material ashes which satisfies that the material bonding is a very important factor in soil stabilization and strength optimization because the soil and the admixture need to form a homogeneous and cohesive bond. Material requirement for cementing materials is that the sum of SiO_2, Al_2O_3, and Fe_2O_3 should not be less than 70%. The result of the analyzed ashes shown in Table 2 shows that the percentage of $SiO_2 + FeO_3 + Al_2O_3$ is greater than 70%, which makes the admixture samples of highly pozzolanic materials except NPKA and NCSA. This property was of great advantage because it brought about a high degree of interaction and bonding between the studied soil samples and the admixtures.

Table 2: Chemical composition test on the selected waste ashes

Ash	CaO %wt	MnO %wt	MgO %wt	ZnO %wt	CuO %wt	Fe_2O_3 %wt	Al_2O_3 %wt	SiO_2 %wt	Na_2O %wt	P_2O_5 %wt	K_2O %wt
NPBA	12.7	0.13	0.01	0.78	Trace	0.95	20.12	64.45	0.71	0.64	0.14
NWTA	12.57	0.13	0.01	3.21	Trace	2.55	31.12	44.45	4.11	1.81	0.04
NWPA	9.21	3.67	Trace	Trace	Trace	1.11	17.23	52.11	7.41	7.99	1.27
NPKA	11.25	4.44	7.86	4.67	12.76	3.89	17.77	23.88	9.01	2.91	1.64
NSSA	17.83	1.16	Trace	Trace	Trace	2.44	6.11	65.01	2.31	5.12	0.02
NCSA	12.31	2.87	7.82	4.66	11.99	3.98	19.89	25.19	9.09	1.11	1.09

From the results of the preliminary tests conducted in our Geotechnical Engineering laboratory tabulated in Table 3, it can be deduced that the disturbed lateritic soil has the following properties;

- A plasticity index of 21.85% > 17% and that condition satisfies that the lateritic soil is a highly plastic soil. Also the plasticity index falls between 20% and 35%, a condition for high swelling potential and between 25% and 41%, a condition for a high degree of expansion [23].
- From the consistency limits tests that the soil relative consistency and liquidity index, which are 1.69% > 1 and 0.91% < 1 respectively show that the soil is in a semi-solid or solid state, very stiff and plastic [23].

- Is classified as A-2-7 soil on AASHTO soil classification, well graded, GW on USCS, the group index of 0 and of silty, clayey gravel and sand material [23].
- Optimum moisture content (OMC) of 13% and maximum dry density (MDD) of 1.84g/cm^3.
- Unconfined Compressive Strength (UCS) of 230.77kN/m^2 at 28 days curing time, which falls between 200 and 400kN/m^2, a condition for soils of very stiff consistency with respect to UCS, which satisfies the material condition for use as sub-grade material [22; 23].
- California bearing ratio of 14 which makes it good for the sub-grade material [22].

Table 3: Geotechnical Properties of the Lateritic Soil Sample

Property/Unit	**Lab Results**	**Standard Condition To BS 1377 [19] and NGS, 1997 [22]**
% Passing BS No. 200 sieve	25.40	% fine particles in the sample
Natural Moisture Content, (%)	10	
Liquid Limit, (LL) (%)	47.00	
Plastic Limit, (PL) (%)	25.15	
Plasticity Index, (PI) (%)	21.85	>17 is highly Plastic
Coefficient of Curvature, $C_c = \frac{{D_{30}}^2}{\mathrm{D}_{10} \times \mathrm{D}_{60}}$	0.09	<1, for well graded sand
Coefficient of Uniformity, $\mathrm{C_u} = \frac{\mathrm{D}_{60}}{\mathrm{D}_{10}}$	10	>5, for well graded silty clay soil
Specific Gravity (G_s)	2.67	2.5 – 2.8 (very stiff)
AASHTO classification	A-2-7	Soil classification for silty Clayey Gravel, sand
USCS	GW	Particle distribution
Group Index	0	
Material	Silty or Clayey Gravel, Sand	
Condition/General Subgrade Rating	Good	Based on the CBR and UCS results
Optimum Moisture Content, (OMC) (%)	13	The higher this gets, the weaker the mixture

Maximum Dry Density (MDD) (g/cm^3)		1.84	
California bearing ratio, (CBR) (%)		14	>10 (good for Sub-grade Material condition)
Unconfined Compressive Strength, (UCS) (KN/m^2)	28 days	230.77	>200 good for Sub-grade material
	14 days	219.11	
	7 days	194.26	
Color		Reddish Brown	

From Figure 7 and Table 3, it can be deduced that the soil is a well graded; this being the distribution of the soil particles in the sample studied, with Cc equals 0.09 and Cu equals 10 (Gopal and Rao, 2011).

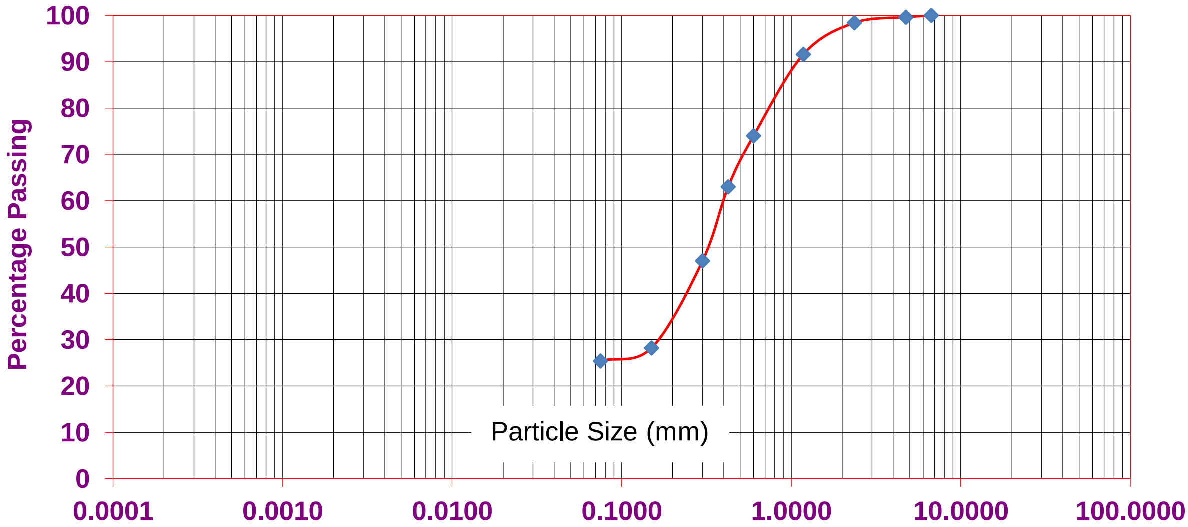

Figure 7: Particle size distribution curve of Umuntu Olokoro lateritic soil sample [3]

The Effect of Nanosized Ashes on the Strength Properties of the Lateritic Soil

Fig 8 shows the CBR behaviour of the stabilized soil with nanostructured ash materials which progressively increased with the addition of the additives. This behavior may be attributed to the admixtures' increased reactive surface area, their highly pozzolanic behavior and lower density as a result of nanosization. With these results, the strength properties of the stabilized soil have been enhanced certifying the ash materials as good construction materials for use in pavements designs and construction. The soil + 12% ash and soil + 15% ash mixtures passed the minimum CBR value of 20 – 30% specified by BS 1924 [20] for materials suitable for use as base course materials when determined at MDD and OMC. This is close to the findings of Gidigasu and Dogbey [7], which stated that the minimum CBR value of 20 – 30% is required for sub-bases when compacted at OMC. Increase in CBR, an implication of the increase observed in MDD is attributed to the compatibility of the grains of soil by the increased reactive surface achieved by the ash pulverization and the high pozzolanic properties of the ashes such that greater densification was achieved.

Figs 9, 10 and 11 show the UCS behaviour of the stabilized soil under the addition of nanostructured ash materials. There was consistent improvement of the UCS with the addition of variable proportions of ash materials. This behaviour is also attributed to the pozzolanic behaviour of the additive and its increased reactive surface that encouraged bonding. A further observation was that the presence of the admixtures in the soil increased the frictional angle of the stabilized mixture attributed to the physicochemical and highly pozzolanic properties of the admixture and to their ability to reduce adsorbed water thereby making soils with higher clay content to behave like granular soil. These values satisfy the "very stiff" material condition for use as sub-base materials for pavement sub-grade and sub-base construction.

The effect of variable proportions by weight (wt) of the nanosized as materials as recorded in Table 4 has shown that the compaction, consistency, and strength behaviours of the lateritic soil improved from the control. The improvements were more remarkable with palm bunch ash and snail shell ash with higher proportions of pozzolanic properties, which had helped in stronger bonding with the soil structure and setting properties of the mixture of soil and the admixture. This may be due to the higher contents of alumina, silicate and ferrite oxides responsible for pozzolanic effects that enhanced bonding and hardening of the stabilized mixture. The dry density increased for all the selected ash materials with the maximum recorded with snail shell ash at 15% by weight of the stabilized mixture. The nanosization of the ashes increased the availability of the pozzolanic properties and calcium ion Ca^{2+} needed for cation exchange reactions in the formation of the silicates, hydrates and aluminates necessary for the densification of the stabilized mixture. The plasticity index achieved with the ash materials maintained a medium plastic consistency, i.e. < 17% away from the control consistency experiment results. The cation exchange may have been enhanced by the nanosization of the solid wastes ashes, which promoted the flocculation of clay particles in the stabilized mass. This is because the nanostructured ash materials had good reactive surface and amorphous property that enabled faster and stronger bonding with the studied soil, thereby improving plasticity. The CBR gave good results that met the requirements for the stabilized soil to be used as a sub-base material in pavement construction. And finally, the unconfined compressive strength test results show great improvements in the stabilized soil with the nanostructured ash materials. The CBR and UCS improved results may be due to the increased reactive surface as a result of nanosization of the amorphous ash materials which encourage the formation of calcium silicate hydrate CSH responsible for densification and hardening of the stabilized soil.

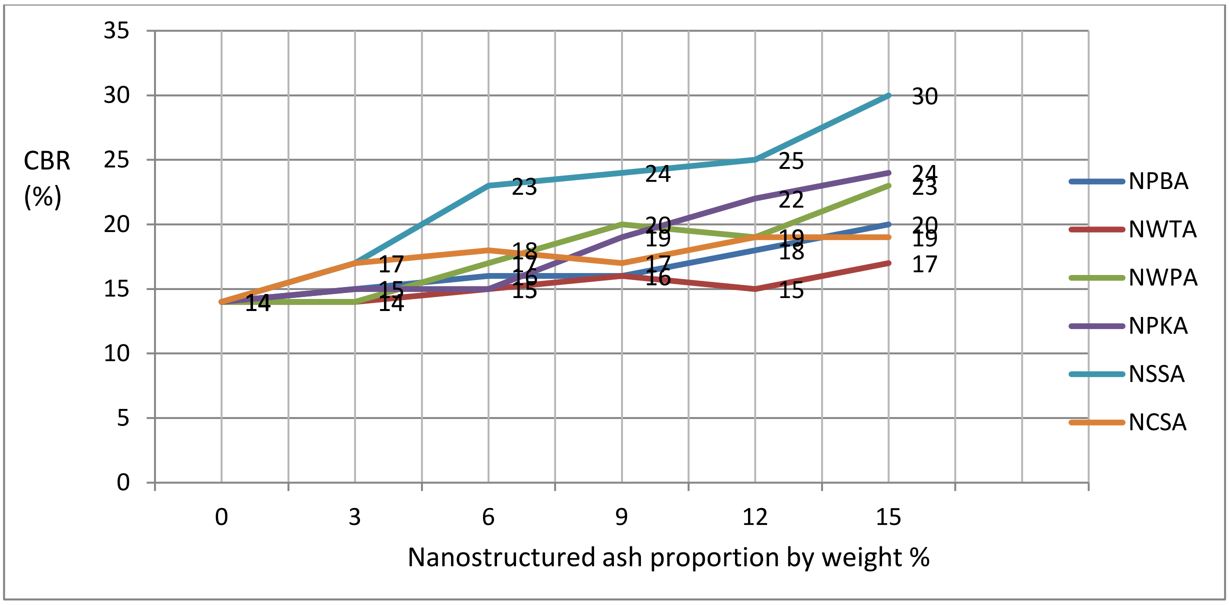

Fig. 8: Stabilized soil CBR behaviour with nanostructured ash materials

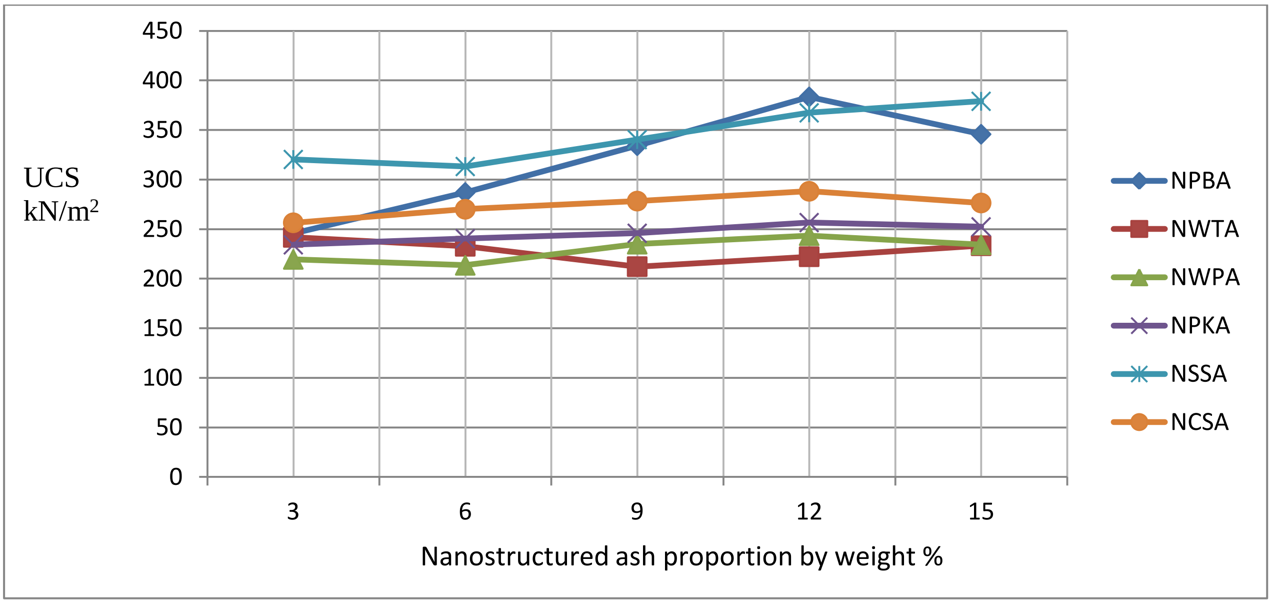

Fig 9: Stabilized soil UCS (7 days curing) behaviour with nanostructured ash materials

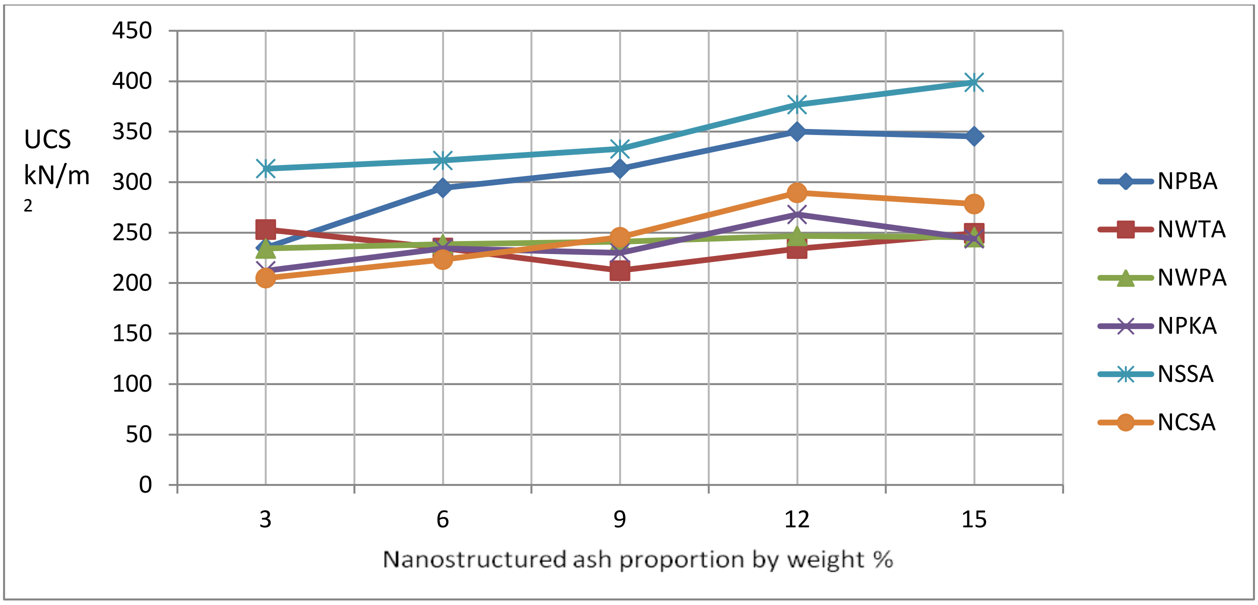

Fig 10: Stabilized soil UCS (14 days curing) behaviour with nanostructured ash materials

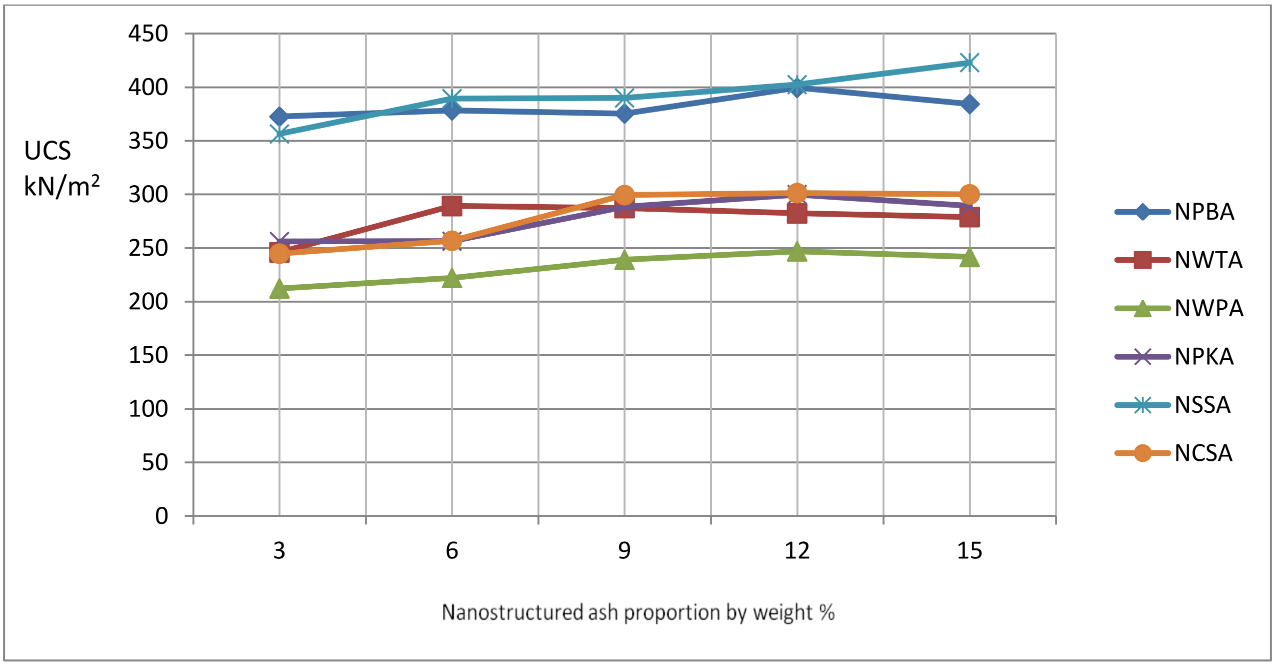

Fig 11: Stabilized soil UCS (28 days curing) behaviour with nanostructured ash materials

Table 4: Behavior of the lateritic soil with the nanosized ashes

Ash	OMC (%)	MDD (g/cm^3)	PI (%)	CBR_{max} (%) @ 2.5mm	UCS_{max} (KN/m^2)		
					7days curing	14days curing	28days curing
NPBA	**11.10** @ 15% by wt	**1.97** @ 15% by wt	**8.21** @ 15% by wt	**20** @ 15% by wt	**383.45** @ 12% by wt	**350.04** @ 12 % by wt	**399.46** @ 12% by wt
NWTA	**10.93** @ 12% by wt	**2.01** @ 12% by wt	**9.45** @ 12 % by wt	**17** @ 12% by wt	**241.77** @ 3% by wt	**253.04** @ 3% by wt	**289.19** @ 6% by wt
NWPA	**10.81** @ 9% by wt	**1.85** @ 9% by wt	**7.5** @ 12% by wt	**23** @ 12% by wt	**243.47** @ 12% by wt	**246.85** @ 12% by wt	**246.99** @ 12% by wt
NPKA	**12.23** @ 12% by wt	**1.89** @ 12% by wt	**11.34** @ 12% by wt	**24** @ 12% by wt	**256.65** @ 12% by wt	**267.99** @ 12% by wt	**299.91** @ 12% by wt
NSSA	**9.88** @ 15% by wt	**2.33** @ 15% by wt	**7.1** @ 15% by wt	**30** @ 15% by wt	**379.01** @ 15% by wt	**398.88** @ 15% by wt	**423.01** @ 15% by wt
NCSA	**13.10** @ 9% by wt	**1.84** @ 9% by wt	**13.22** @ 9% by wt	**19** @ 12% by wt	**288.24** @ 12% by wt	**289.45** @ 12% by wt	**301.22** @ 12% by wt

4. Conclusion

From the foregoing, it can be concluded as follows;

- The application of ashes synthesized from these solid wastes suggests an efficient method of ridding the environment of the pollutants.
- That the solid waste materials were locally synthesized and characterized using the spectrophotometric UV-VIS method which established the average particle sizes of the ashes and confirmed them as nanosized particles.
- That the absorbance and increased reactive surface of the ash materials played a big role at the reactive phase between the ash materials and the lateritic soil to improve the van der waal's forces of the treated matrix.
- That the compaction, consistency limits and strength properties behaviour of the stabilized lateritic soil improved remarkably at different percentages of the ash materials by weight (wt) of stabilized mixture.
- That through this reuse of solid waste materials in Environmental and Transportation Geotechnics, the management and disposal of solid waste in Nigeria must have received a boost and the Federal and State Ministries of Environment and Works

should key into these findings to improve on waste management, pavement rehabilitation and engineering and re-engineering.

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